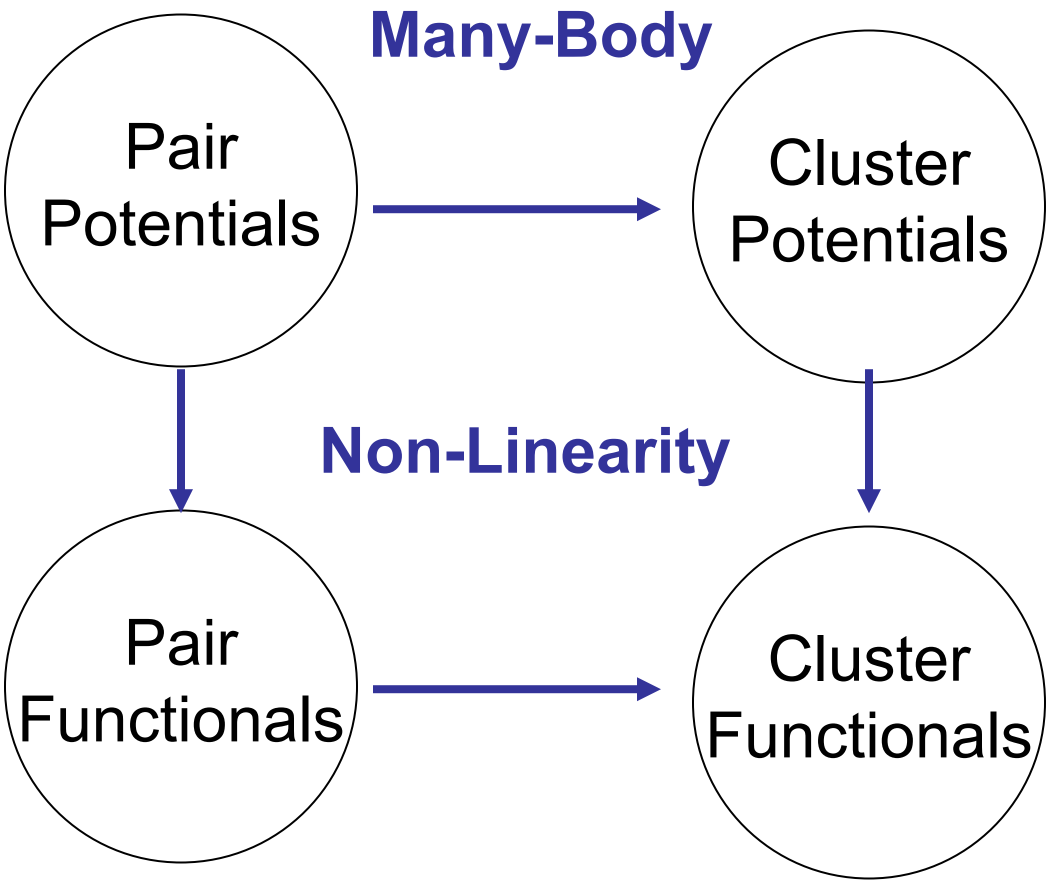
Atomistic Modeling of Materials

Potentials for Organic Materials and Oxides

3.320 Lecture 3a (2/8/05)

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

How to Fix Pair Potential Problem ?



Many-Body

Pair Potentials

Cluster Potentials

Non-Linearity

Pair Functionals

Cluster Functionals

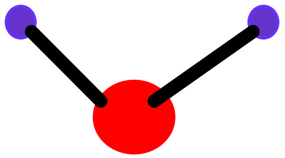
Organic Molecules and Polymers

Distinguish between **BONDED** and **NON-BONDED** interactions

Along covalent bonds

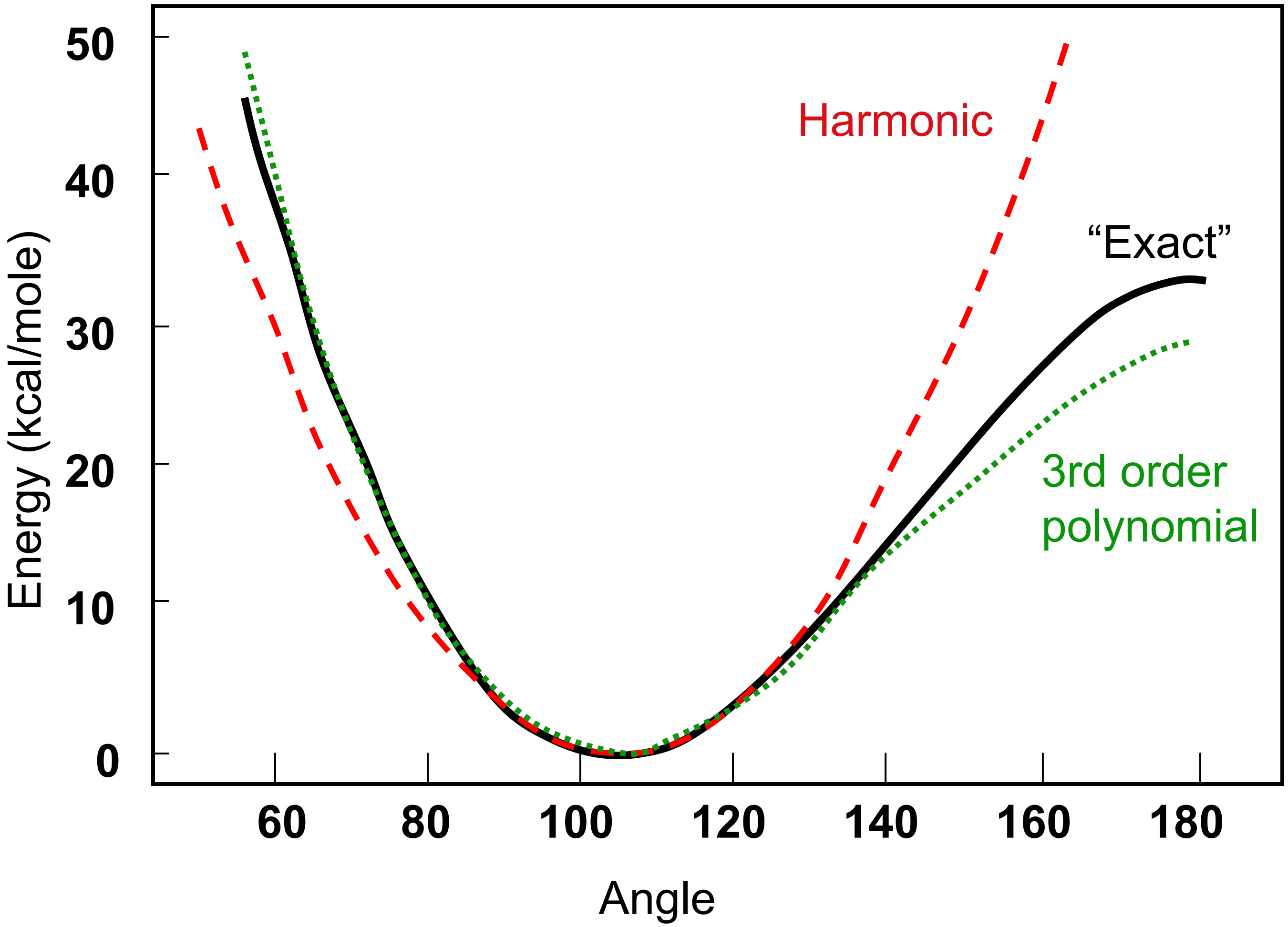
Between atoms that are not bonded

Example: A Potential for H$_2$0: Relevant Energy Terms



In class exercise: please take notes

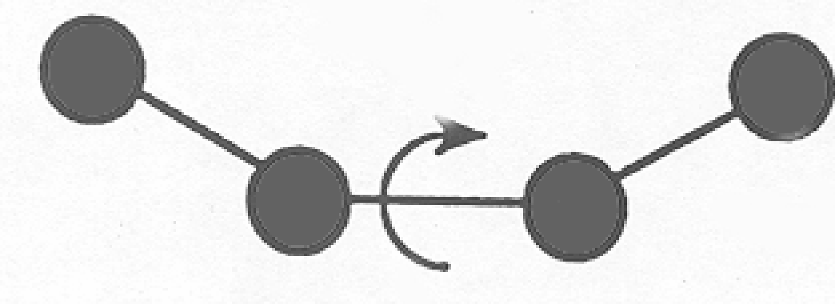
Bending term for H_20



More complicated molecules

Example: Ethane: Staggered versus Eclipsed configuration has different energy:

⇨ *Need four-body potential*

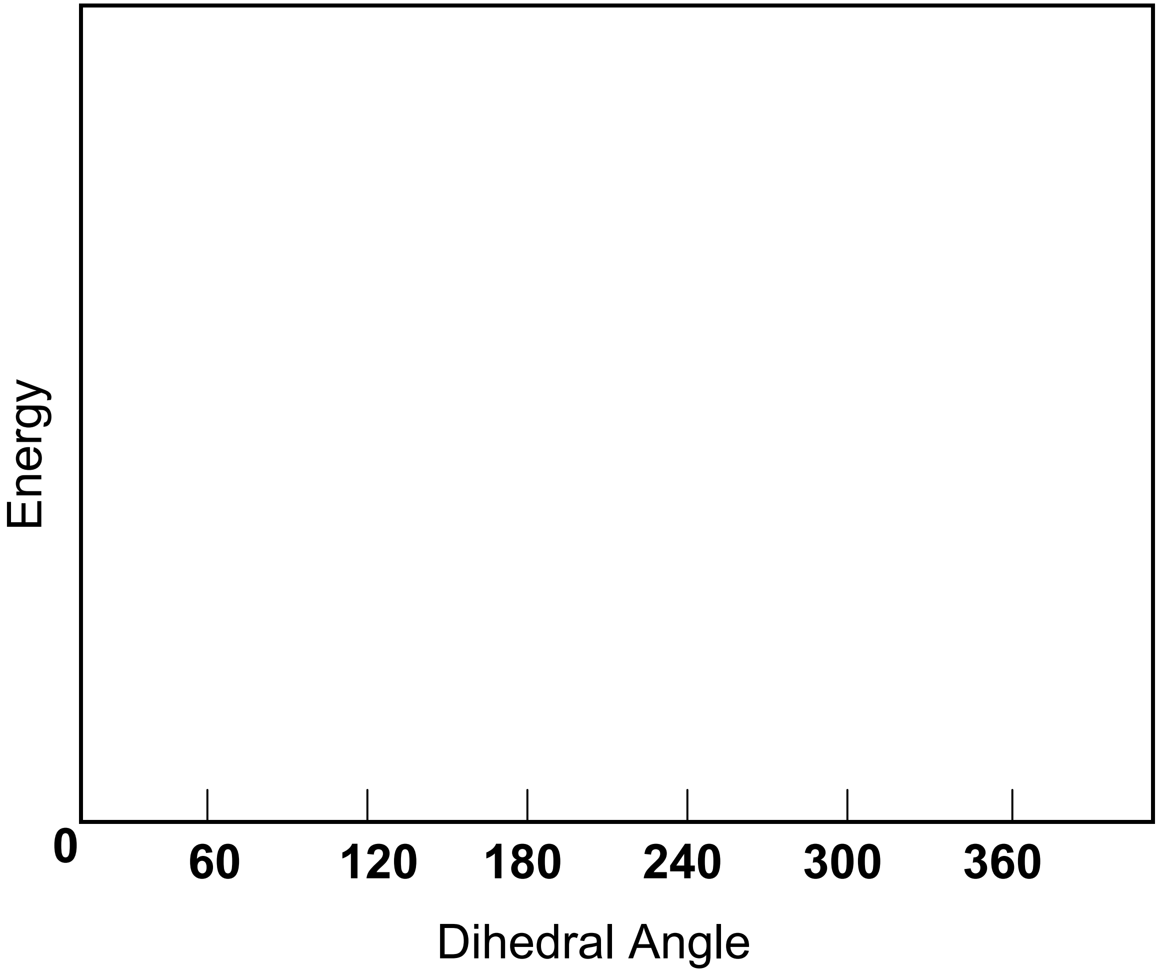


Periodicity requirements: e.g for ethane configurations repeat after 120 degrees torsion

torsion angle

$$V_{\text{torsion}} = K \cos (3\omega)$$

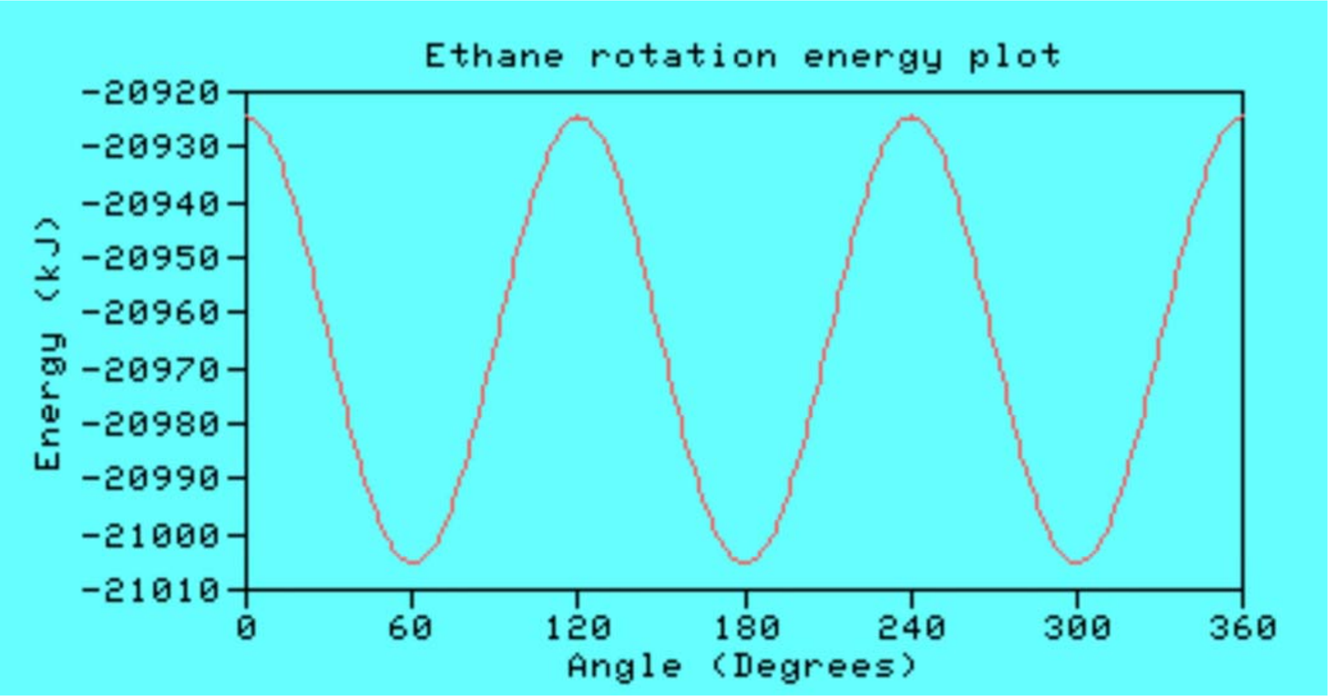
Torsion Potential has Periodicity



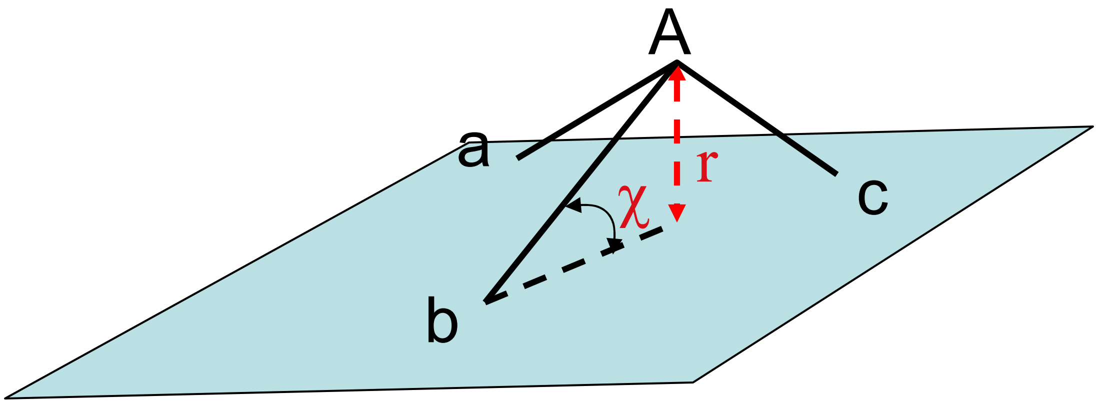
Draw cos(2ω)

and cos(3ω)

Torsion Potential has Periodicity



Out-of-Plane or Improper Torsion

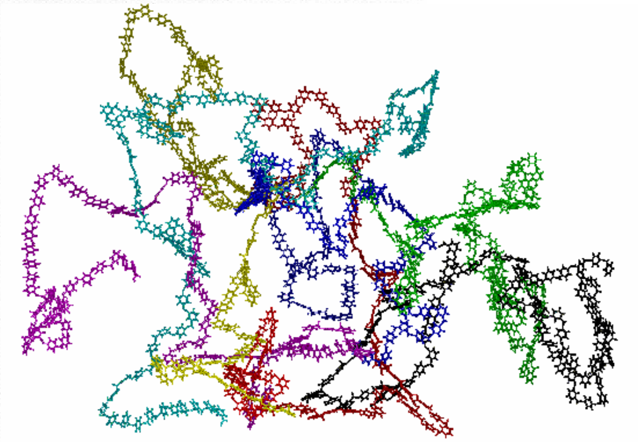


Used when the four atoms defining the torsion are “not in sequence”

A real example: Poly-Hydroxybenzoic Acid

$$\mathcal{U} = \sum_{chains} \{ \sum_{ijk} \mathcal{U}_{valence,ijk} + \sum_{ijkl} \mathcal{U}_{torsion,ijkl} + \sum_{ijkl} \mathcal{U}_{improper\ torsion,ijkl} + \frac{1}{2} \sum_{ij} \mathcal{U}_{vdW,ij} + \frac{1}{2} \sum_{ij} \mathcal{U}_{Coulomb,ij} \}$$

where



$$\begin{aligned}
\mathcal{U}_{valence,ijk} &= \frac{1}{2} k_v (\theta_{ijk} - \theta_{ijk,0}) \\
\mathcal{U}_{torsion,ijkl} &= \sum_{m=1}^{4} H_{m\phi}(1 - cos(m\phi_{ijkl})) \\
\mathcal{U}_{improper\ torsion,ijkl} &= H_{2\Phi}(1 - cos(2\Phi_{ijkl})) \\
\mathcal{U}_{vdW,ij} &= 4\epsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}] \\
\mathcal{U}_{Coulomb,ij} &= (4\pi\epsilon_o r_{ij})^{-1} q_i q_j .
\end{aligned}$$

Why do potentials work so well in organics ?

One given potential does not deal with changes in the coordination of covalent bonds. Changes in coordination are done by changing the potential ! ->

Hence: different potentials for sp^2, sp^3 sp carbon …

Potentials good for:

- ☐ Conformation (configuration) of molecules
- ☐ Packing of molecules
- ☐ Barriers between various conformations

Potentials not good for:

- ☐ Chemical reactions (bond breaking)

Potentials lack polarization

Many general potential parameterizations for common organic molecules

Table removed for copyright reasons.

a set of good links for empirical models in chemistry

http://www.msg.ku.edu/~msg/MGM/links/ffield.html

Empirical Models in Oxides

Well developed field. Relatively successful

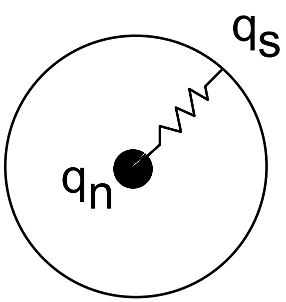
Typically, Buckingham + electrostatic term is used

$$V(r) = A\exp\left[-\frac{r}{\rho}\right] - \frac{C}{r^6} + \frac{q_1 q_2}{r}$$

long-ranged electrostatic part is summed by Ewald method

Polarization: induced dipole from electrical field from other ions

Shell Model



$q_n + q_s = q_{ion}$

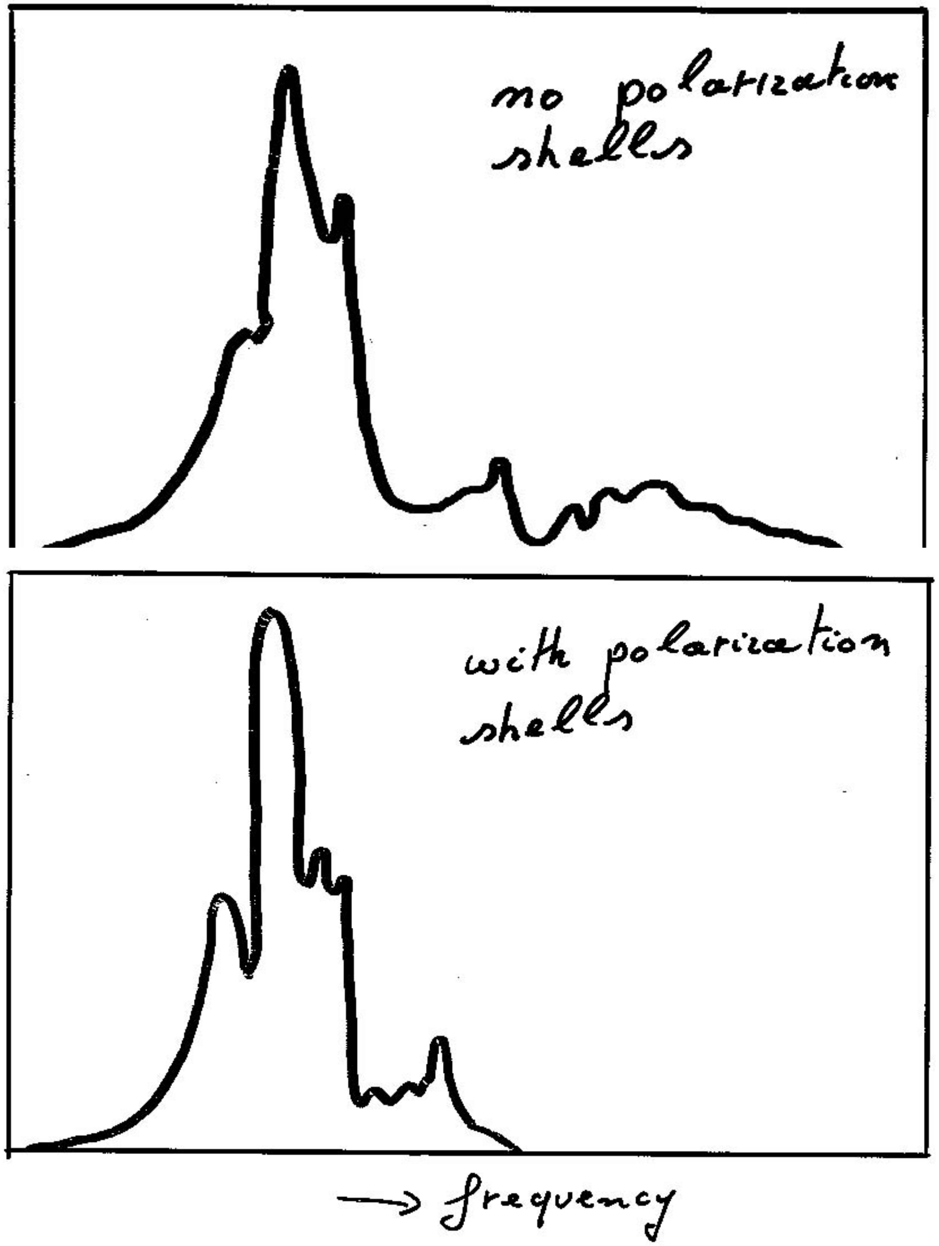
Two particles used per ion: **core** and **shell**, connected by a spring

- Shell interacts with other shells through potentials
- Cores and shells interact eletrostatically
- Core and shell of one atom are coupled through a spring

$$V_{ion} = k\Delta r^2$$

spring constant *k* relates to polarizability of the ion

Phonon density of states of MgO



A good source for potentials in oxides

Self-Consistent Interatomic Potentials for the Simulation of Binary and Ternary Oxides

Bush, T. S., J. D. Gale, R. A. Catlow, and P. D. Battle, 1994: . *Journal of Materials Chemistry*, **4,** 831-837.

A consistent set of pair potentials has been derived empirically by fitting to the experimentally measured lattice properties of a series of binary metal oxide. In contrast to previous strategies, the potential parameters were optimized concurrently, utilizing residuals from all structures in the series, each calculated from the energy-minimized geometry. A more reliable determination of ion polarisabilities can thus be made.

Good source for oxide potentials on the web collected by Woodley:

http://www.ri.ac.uk/DFRL/research_pages/resources/Potential_database/index.html

Limitations of Pair Potentials in Oxides

Oxygen Breathing Effects

oxygen ion changes size as function of its environment

Variable Charge Effects

Especially transition metal ions have charge state dependent on environment

Multibody Bonding Effects

Evaluation of Potentials

For metals

Bond energy depends very much on the number of bonds already made to an atom. Such an effect is absent in pair potentials, which are by definition environment-independent.

As a result, whenever bond-breaking in covalent materials is involved, the result of a potential model should be interpreted cautiously.

For organic molecules

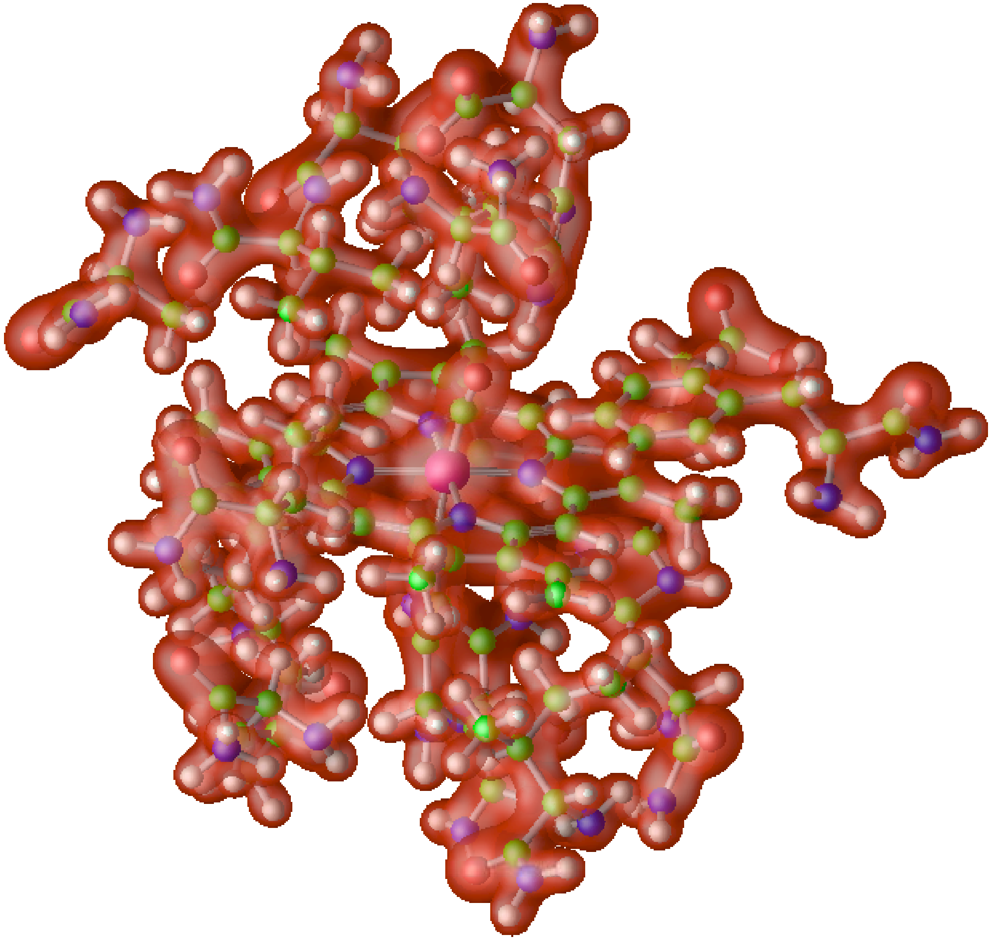
Very good potentials have been fit to C-H and C-C bonds in various bonding arrangements. These can be used to model conformational arrangements of polymeric systems (where no bond-breaking is involved)

For oxides

In highly ionic oxides, qualitatively reasonable results can be expected with empirical potential models (+ electrostatic energy). Accuracy is mainly limited by the oxygen "breathing" effect. The more covalent the oxide, the more difficult it will be to find potentials that reproduce the materials behavior in a wide range of environments. Shell polarization is essential in low symmetry environments.

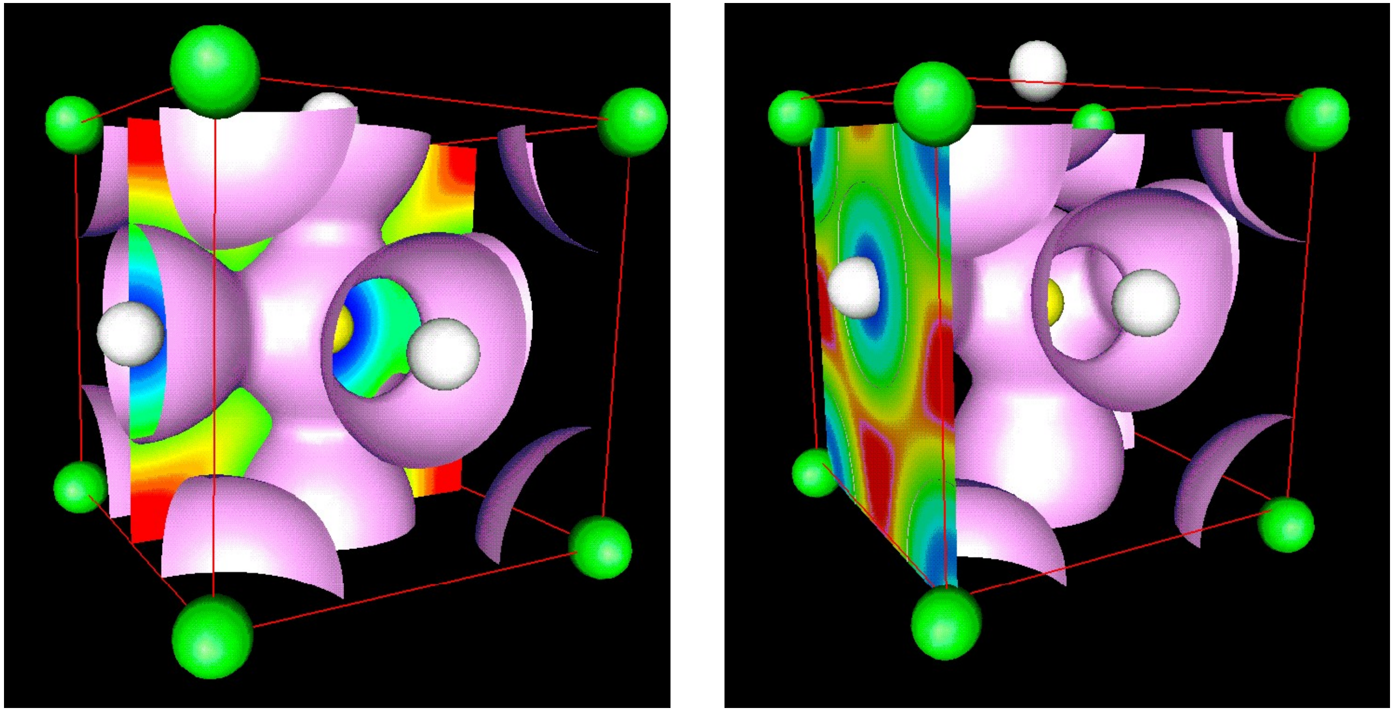
3.320: Lecture 3b (Feb 8 2005)

IT'S A QUANTUM WORLD !



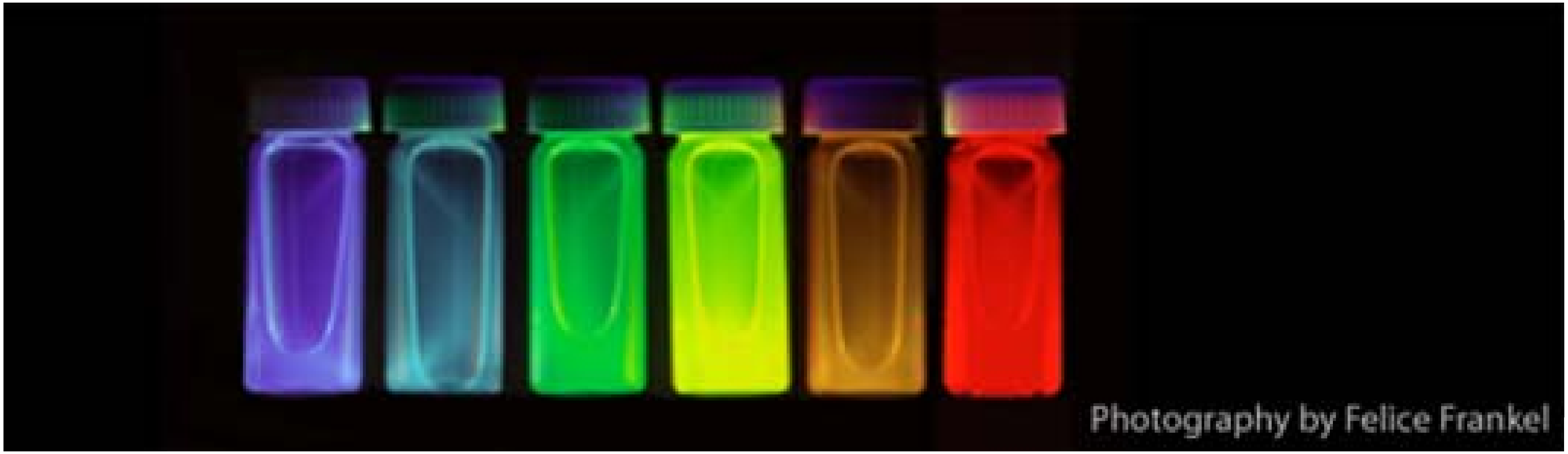
Why do we need quantum mechanics ?

1) Bonding and Structure



Paraelectric (cubic) and ferroelectric (tetragonal) phases of $PbTiO_3$

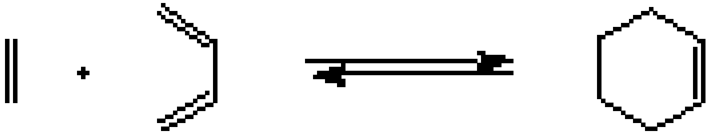
2) Electronic, optical, magnetic properties



Courtesy of Felice Frankel. Used with permission.

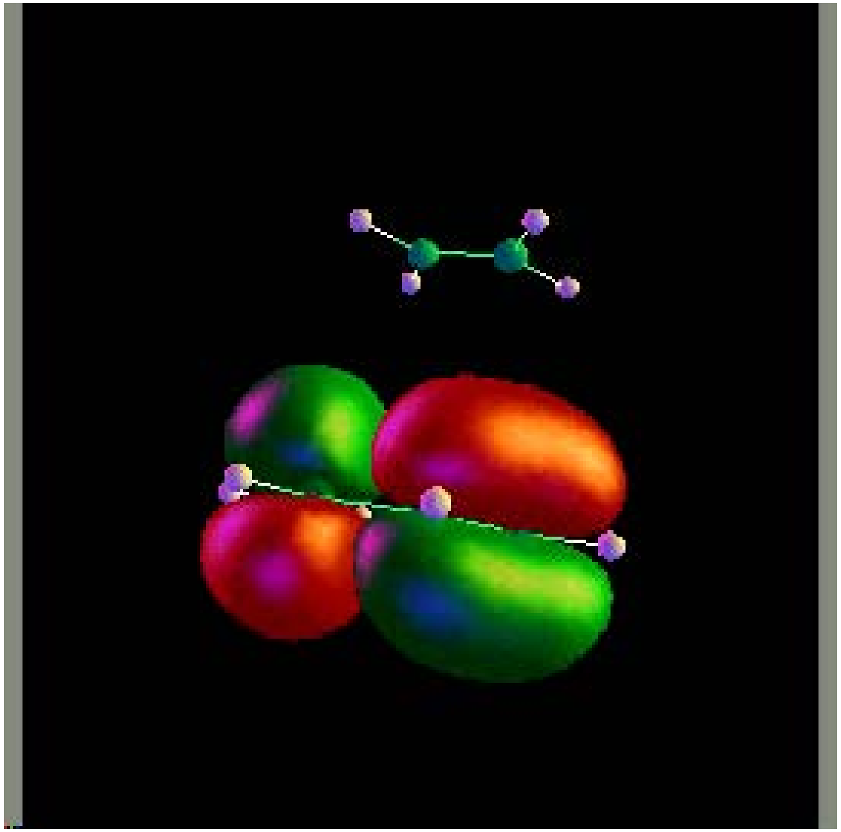
3) Dynamics, chemistry

Diels-Alder Reaction:
1,3-butadiene + ethylene → cyclohexene



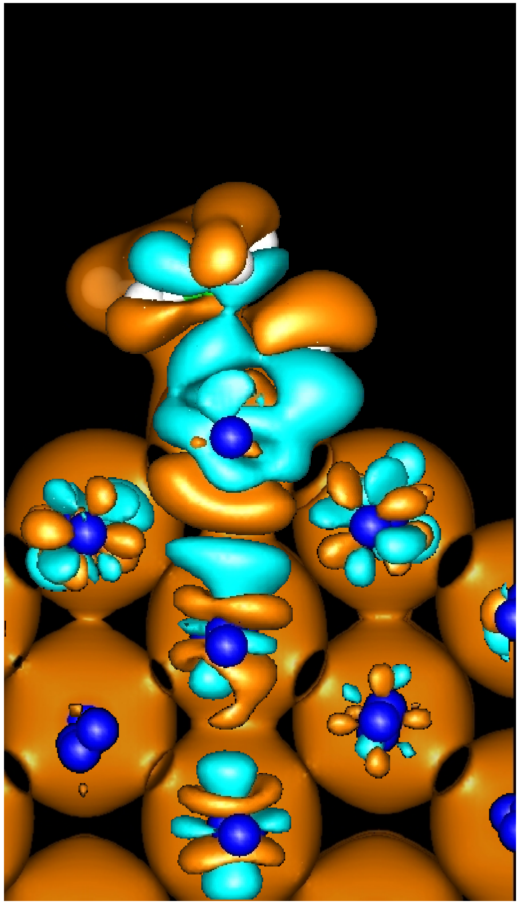
http://www.wag.caltech.edu/home-pages/jim/

Courtesy of James Kendall. Used with permission.



Standard Model of Matter

- Atoms are made by massive, point-like nuclei (protons+neutrons)
- Surrounded by tightly bound, rigid shells of core electrons
- Bound together by a glue of valence electrons



Material Properties From First-Principles

- Energy at our living conditions (300 K): 0.04 eV (kinetic energy of an atom in an ideal gas: 3/2 $k_B T$).
- Differences in bonding energies are within one order of magnitude of 0.29 eV (hydrogen bond).
- Binding energy of an electron to a proton (hydrogen): 13.6058 eV = 1 Rydberg (Ry) = 0.5 Hartree (Ha) = 0.5 a.u

Bibliography

- Richard M. Martin, *Electronic Structure: Basic Theory and Practical Methods,* Cambridge University Press (2004).
- Mike Finnis, *Interatomic Forces in Condensed Matter*, Oxford University Press (2003).
- Efthimios Kaxiras, *Atomic and Electronic Structure of Solids*, Cambridge University Press (2003).

Courtesy of The Reduced Shakespeare Company. Used with permission.

Wave-particle Duality

- *Waves have particle-like properties:*
  - *Photoelectric effect: quanta (photons) are exchanged discretely*
  - *Energy spectrum of an incandescent body looks like a gas of very hot particles*
- Particles have wave-like properties:
  - Electrons in an atom are like standing waves (harmonics) in an organ pipe
  - Electrons beams can be diffracted, and we can see the fringes

When is a particle like a wave ?

Wavelength • momentum = Planck

$$\updownarrow$$

$\lambda \bullet p = h$ ($h = 6.6 \times 10^{-34}$ J s)

http://www.kfunigraz.ac.at/imawww/vqm/

Quantum effects in the nuclear motion

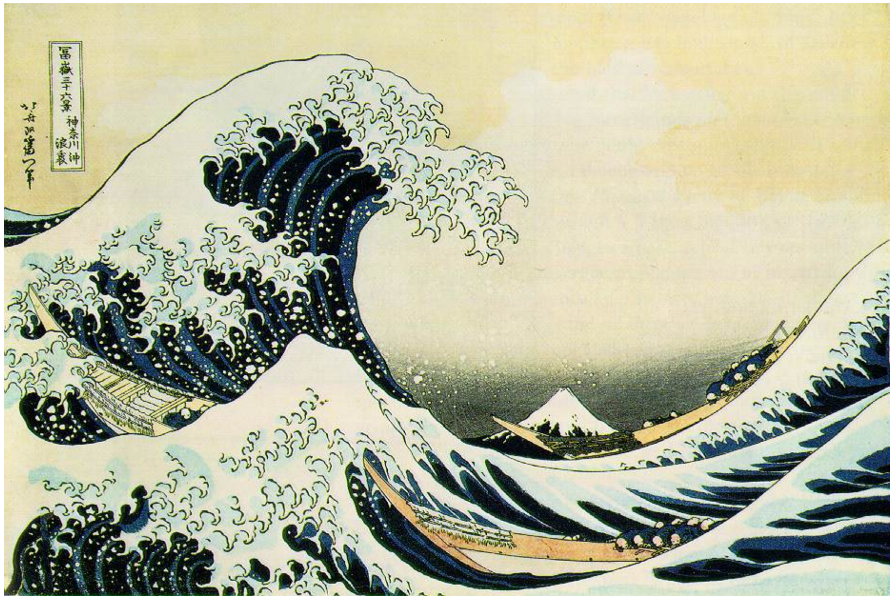
“The nature of the hydrated excess proton in water”, Marx, D., Tuckermann, M. E., Hutter, J., & Parrinello, M. (1999). Nature (London) 397, 601-604

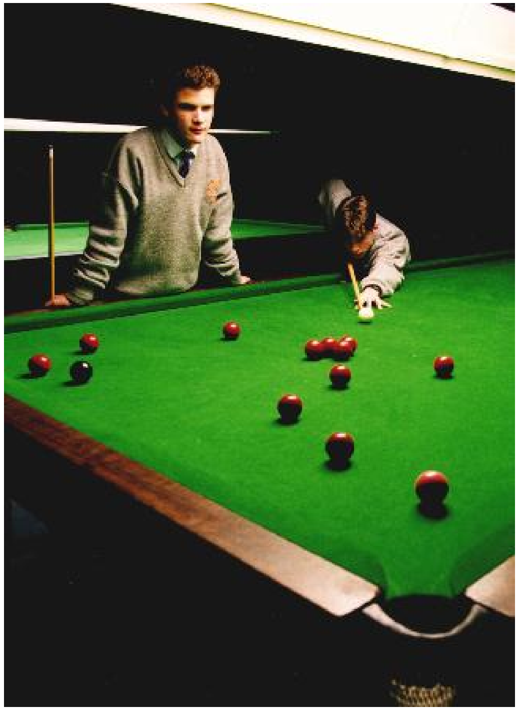
Pair of graphs removed for copyright reasons.
Source: Marx et al, Nature 1999 as above.

“Effect of Quantum Fluctuations on Structural Phase Transitions in $SrTiO_3$ and $BaTiO_3$”, W. Zhong and David Vanderbilt, Phys.Rev. B 53, 5047 (1996)

So, What Is It ? A Misnomer…

It’s the mechanics of waves, instead of classical particles





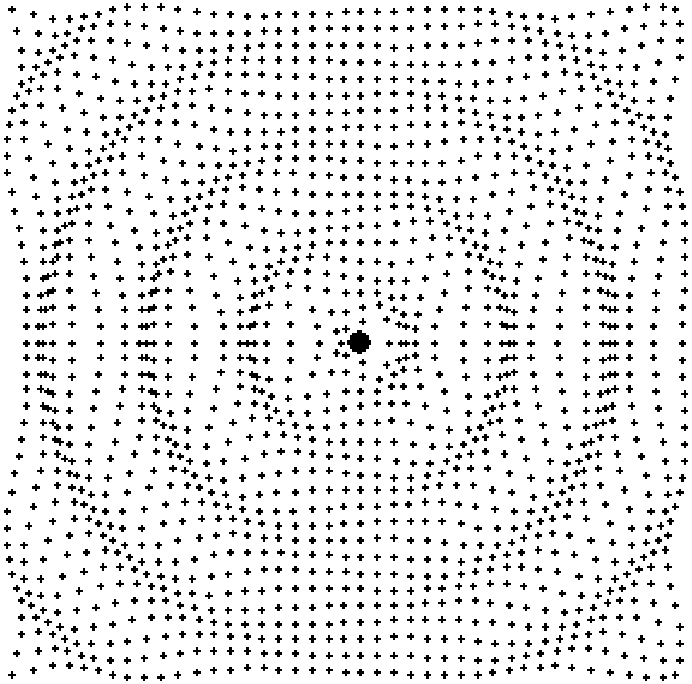
Mechanics of a Particle

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}(\vec{r}) = -\vec{\nabla}V(\vec{r}) \longrightarrow \begin{matrix}\vec{r}(t)\\[1em] \vec{v}(t)\end{matrix}$$

The sum of the kinetic and potential energy is conserved

Image removed for copyright reasons.
Cannon firing a cannonball.

Description of a Wave



The wave is an excitation (a vibration): we need to know the amplitude of the excitation at every point and at every instant

$$\Psi = \Psi(\vec{r}, t)$$

Time-dependent Schrödinger's equation

(Newton's 2nd law for quantum objects)

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},t)\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}}$$

1925-onwards: E. Schrödinger (wave equation), W. Heisenberg (matrix formulation), P.A.M. Dirac (relativistic)

Stationary Schrödinger's Equation (I)

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{r},t)+V(\vec{r},\cancel{t})\Psi(\vec{r},t)=i\hbar\frac{\partial\Psi(\vec{r},t)}{\partial t}$$

Stationary Schrödinger's Equation (II)

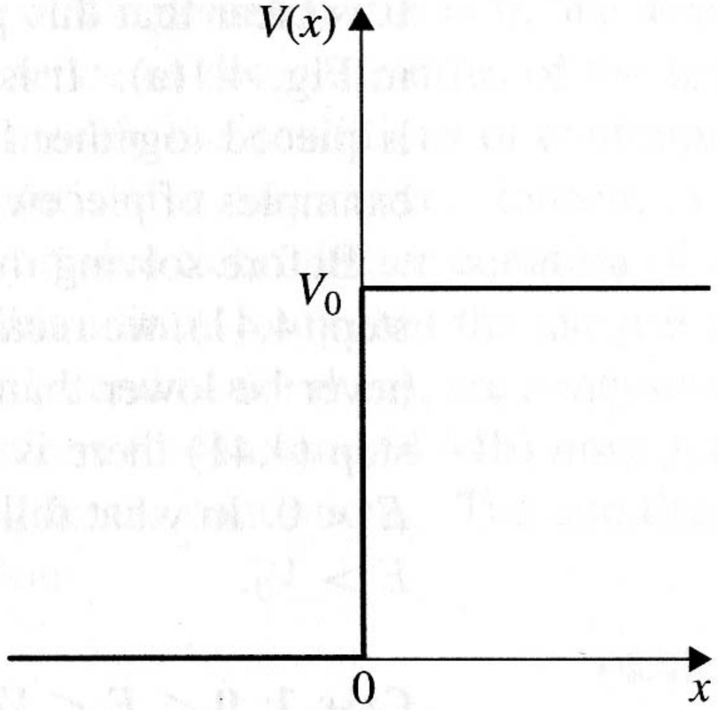
$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right]\varphi(\vec{r})=E\varphi(\vec{r})}$$

Interpretation of the Quantum Wavefunction (Copenhagen)

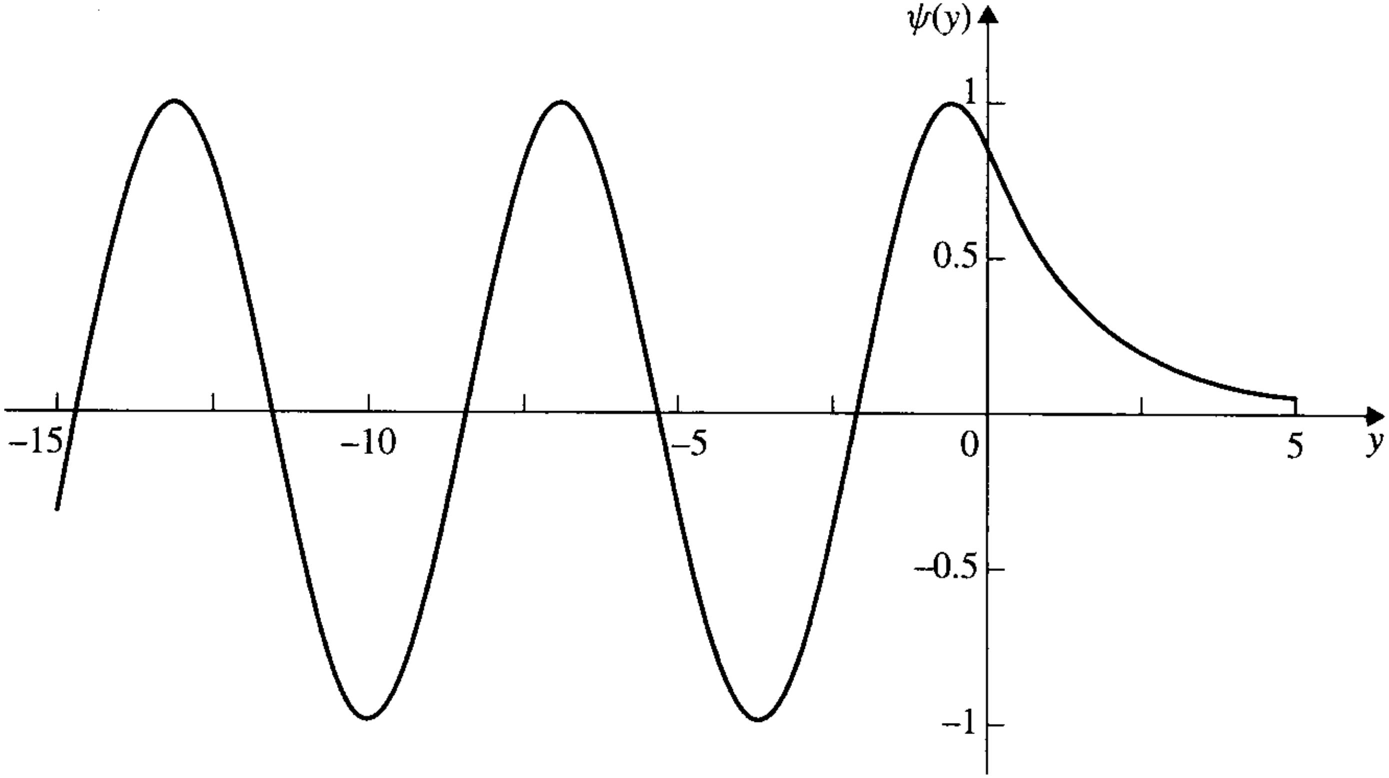
$\left\| \Psi(\vec{r}, t) \right\|^2$ is the probability of finding an electron in *r* and *t*

$$\left\| \varphi(\vec{r}) \exp\left(-\frac{i}{\hbar} Et\right) \right\|^2 = \left\| \varphi(\vec{r}) \right\|^2$$

Metal Surfaces (I)

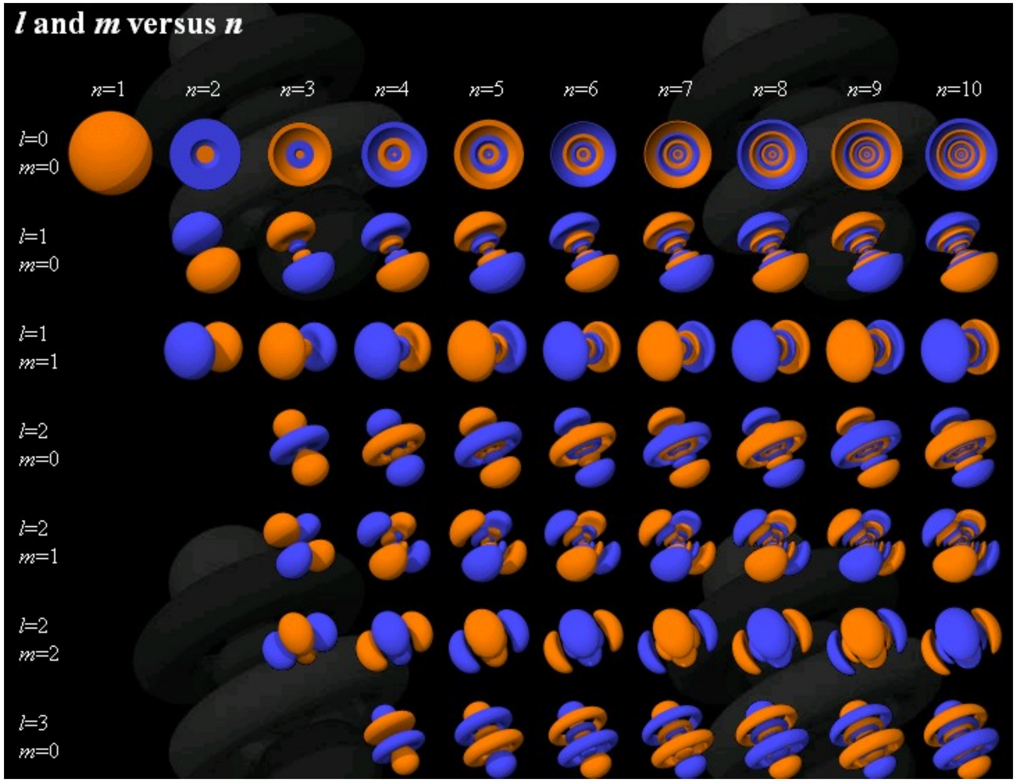


Metal Surfaces (II)



Solutions in a Coulomb Potential: the Periodic Table

http://www.orbitals.com/orb/orbtable.htm



Courtesy of David Manthey. Used with permission.